Exocyclische en endocyclische dubbele binding bij adamantaan

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SUMMARY.

This thesis deals with exocyclic and endocyclic double bond formation with respect to adamantane, 1. The adamantane skeleton is rigid and the dihedral angle between the primary and secundary hydrogenatoms is large, 1a.

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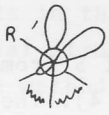
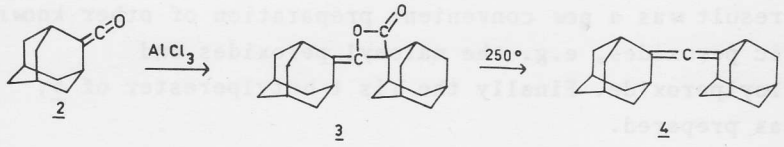


As a result of this the migratory aptitude of the bridgeheadhydrogenatoms is absent and conversion of 1-adamantylkation and 2-adamantylkation proceeds via intermolekulair hydrogenexchange (chapter 1). This property together with the steric behaviour of the adamantane moiety is utilized to stabilize reactive functional groups and small ring compounds (chapter 2). The ability to form crystalline derivates is an extra advantage. Reactions of the keten 2-carbonyladamantane 2 are studied, e.g. ozonisation to an α-lacton, addition of diazomethane to a cyclopropanon and spirocyclobutanones. The diondimeer of 2 is found to be unreactive. Despite the fact that it is highly hindered the keten 2 can be dimerized with alumimum chloride catalyst to the lactondimer 3. Flash pyrolysis of this compound leads to the allene bis-adamantylidene methane 4. The allene oxide derived from 4 is proven to be stable.



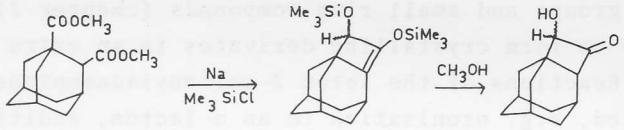
2 3 4

The question of the possibility of an endocyclic double bond in the adamantane nucleus is posed against the background of the modern version of Bredt's rule (chapter 3).

A conception of 1,2-dehydroadamantane or "adamantene" 5 as a transient reaction intermediate is proposed. On the basis of this idea attempts were made to synthesize

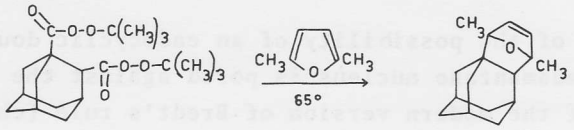
5

suitable precursors of 5 from 1,2-adamantanedicarboxylic acid 6 (R=H) (chapter 4). The acyloïn condensation of the dimethylester 6 ($R=CH_3$) gave an unexpected result. The aforementioned large dihedral angle and the rigidity of the skeleton do not allow the C_3 and C_4 carbonatoms in 7 to be sp^2-hybridized simultaneously. The double bond is shifted to the 2,3 position in order to relief strain.



6 7 8

The acyloin 8 cannot be oxidized to the corresponding dion, which would be a possible precursor of adamantene. The idea of oxidative degradation of the diacid 6 to generate adamantene under mild conditions leaded to the search of so-called peroxyprecursors. Attempts to synthesize a six-membered ring cyclic peroxide from 6 were unsuccessfull. The result was a new convenient preparation of other known cyclic peroxides, e.g. the malonyl peroxides and phtaloylperoxide. Finally the bis t-butylperester of 6, 9, was prepared.



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Decomposition of the bisperester 9 at 70°C in the presence of 2,5-dimethylfuran gave a complex mixture, from which in 9% yield the compound was isolated, which we assigned structure 10. This is a very strong indication of the existence of intermediate adamantene. However, in this procedure a stepwise decomposition-addition mechanism cannot be definitely excluded. An evaluation of this results with recent developments in this field closes this thesis. A new formal dipolar structure of some anti-Bredt alkenes based on the method of generation is proposed.

The most important results of this research are published in the English language in international journals.[39,53, 125, 108, 173, 189].